

# **Advanced Hydrogen/Methanol Utilization Technology Demonstration**

## **Phase II: Hydrogen Cold Start of a Methanol Vehicle**

Hydrogen Consultants, Inc.  
*Littleton, CO*

NREL technical monitor:  
C. Colucci



National Renewable Energy Laboratory  
1617 Cole Boulevard  
Golden, Colorado 80401-3393  
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## **1.0 Introduction and Executive Summary**

This is the Phase II Final Report on NREL Subcontract No. XR-2-11175-1 "Advanced Hydrogen/Methane Utilization Demonstration" between the National Renewable Energy Laboratory (NREL), Alternative Fuels Utilization Program, Golden, Colorado and Hydrogen Consultants, Inc. (HCI), Littleton, Colorado. Mr. Chris Colucci was NREL's Technical Monitor. Colorado State University's (CSU) Engines and Energy Conversion Laboratory was HCI's subcontractor. Some of the vehicle test work was carried out at the National Center for Vehicle Emissions Control and Safety (NCVECS) at CSU. The collaboration of the Colorado School of Mines is also gratefully acknowledged.

Hydrogen is unique among alternative fuels in its ability to burn over a wide range of mixtures in air with no carbon-related combustion products. Hydrogen also has the ability to burn on a catalyst, starting from room temperature. Hydrogen can be made from a variety of renewable energy resources and is expected to become a widely used energy carrier in the sustainable energy system of the future.

One way to make a start toward widespread use of hydrogen in the energy system is to use it sparingly with other alternative fuels. The Phase I work showed that strong effects could be achieved with dilute concentrations of hydrogen in methane (11). Reductions in emissions greater than the proportion of hydrogen in the fuel provide a form of *leverage* to stimulate the early introduction of hydrogen. Per energy unit or per dollar of hydrogen, a greater benefit is derived than simply displacing fossil-fueled vehicles with pure hydrogen vehicles.

### **1.1 Hydrogen Cold-Start**

The Phase II work pursued even greater leverage by using hydrogen with methanol. Methanol, like all liquid fuels, produces most of its toxic and photochemically reactive exhaust emissions during the first few minutes after a "cold" motor vehicle is started. These "cold-start" emissions can be greatly reduced by starting the vehicle on hydrogen. In the ultra leanburn mode ( $\lambda \approx 3$ ), a hydrogen fueled engine's exhaust is very clean and has a high oxygen concentration.

### **1.2 Hydrogen Heated Catalyst**

After a methanol vehicle reaches operating temperature it depends on a three-way catalyst for emissions control. The amount of time required for the catalyst to reach operating temperature may be reduced by actively heating it, rather than waiting for the exhaust to do so. In addition to starting and idling the engine on hydrogen, additional hydrogen was injected into the oxygen-rich exhaust stream. The hydrogen and oxygen burned on the surface of the catalyst, heating it directly. A chemical heating power of 15.1kW was applied in the tests discussed below.

### **1.3 Emissions Test Results**

The benefits of hydrogen cold-start and heating the catalyst with hydrogen were investigated using Phase I of the Federal Light-Duty Vehicle Emissions Test (FTP).

These tests, commonly called "Cold 505s," were conducted with CSU's award-winning Methanol Marathon competition vehicle. The usual battery of instrumentation in the NCVECS laboratory was supplemented by a Fourier Transform Infrared (FTIR) analyzer.

A baseline for comparison was generated with back-to-back Cold 505s on M85 (15% unleaded gasoline in methanol). M85 was used because the vehicle is difficult to start on pure methanol; the long cranking time and frequent stalls make methanol cold-start test repeatability virtually impossible. In addition, the methanol emissions are very high until the engine reaches operating temperature. Although the balance of the hydrogen cold-start testing was conducted with neat methanol (M100), the M85 baseline still provides a realistic basis of comparison for a new cold-start technique against the most common method.

The results are shown in Figure 1-1, relative to the M85 baseline. The hydrogen cold-start reduced carbon monoxide by 35% and nitrogen oxides by 3% on NCVECS instrumentation. The FTIR showed total hydrocarbon (THC) emissions reduced by 71%, an 8% reduction in unburned methanol, and a 4% reduction in aldehyde emissions.

The cumulative benefits of cold-starting on hydrogen and using hydrogen to heat the catalyst were a 44% reduction of carbon monoxide and a 17% reduction in nitrogen oxides, according to NCVECS standard instrumentation. The FTIR showed a 79% reduction in total hydrocarbons, 76% reduction in unburned methanol, and an 18% decrease in aldehydes.

#### **1.4 Hydrogen Leverage**

The improvements shown in Figure 1-1 were accomplished with less than 1% hydrogen fuel, in the case of cold-start only, and just over 2% hydrogen fuel including the amount used to heat the catalyst. Leverage factors indicate how much the clean burning properties of hydrogen are amplified, relative to burning an equal amount of hydrogen in a vehicle that produces virtually zero emissions. The leverage factors (see Figure 1-2) are obtained by dividing the percent emissions reductions by the percent of the total fuel energy supplied as hydrogen.



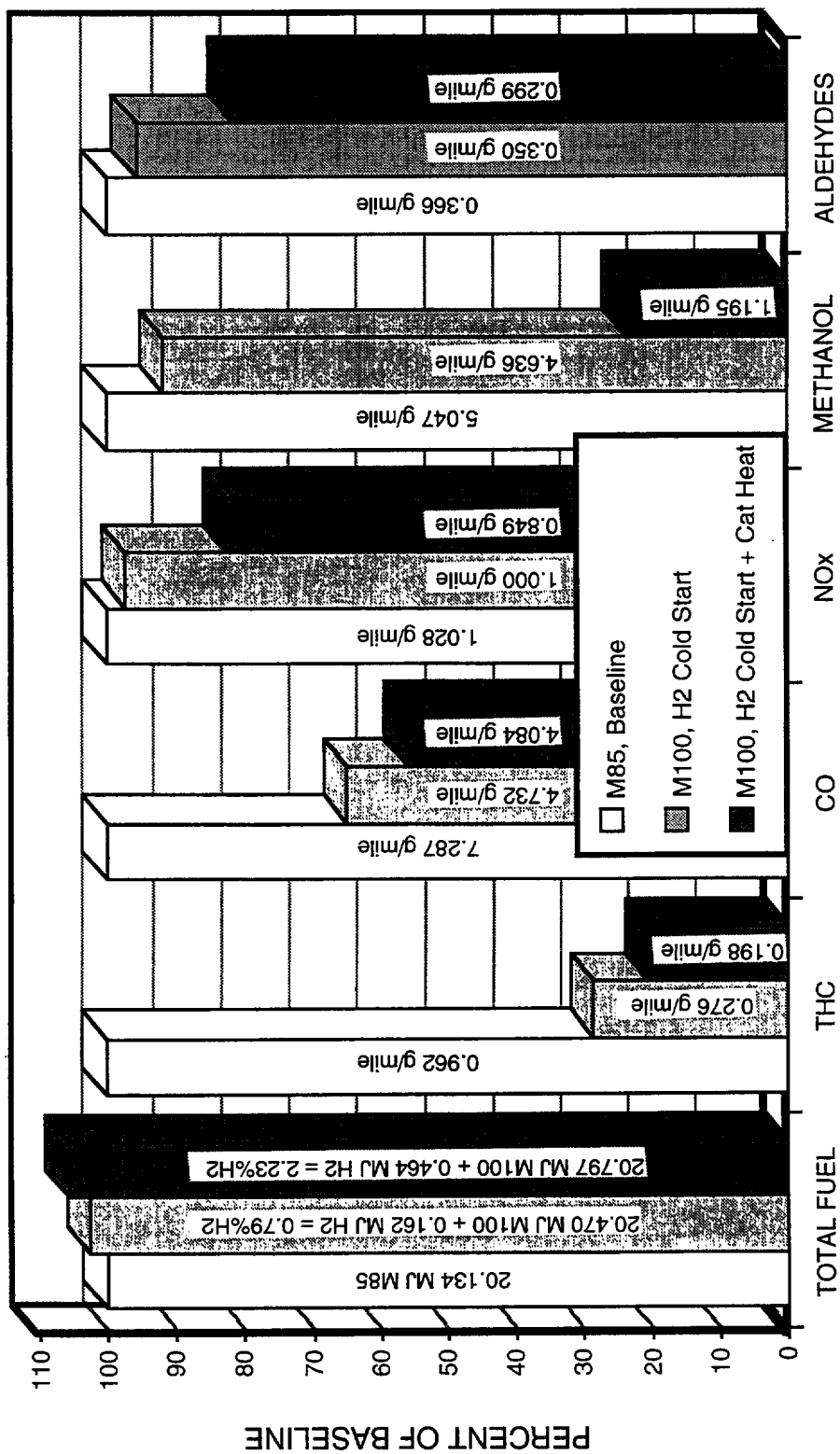


Figure 1-1. Comparison of Cold 505 tests: an M85 baseline test, an M100 test with the first 20 seconds of operation on pure hydrogen, and another M100 hydrogen cold start test with additional hydrogen injection into the exhaust to heat the catalyst.

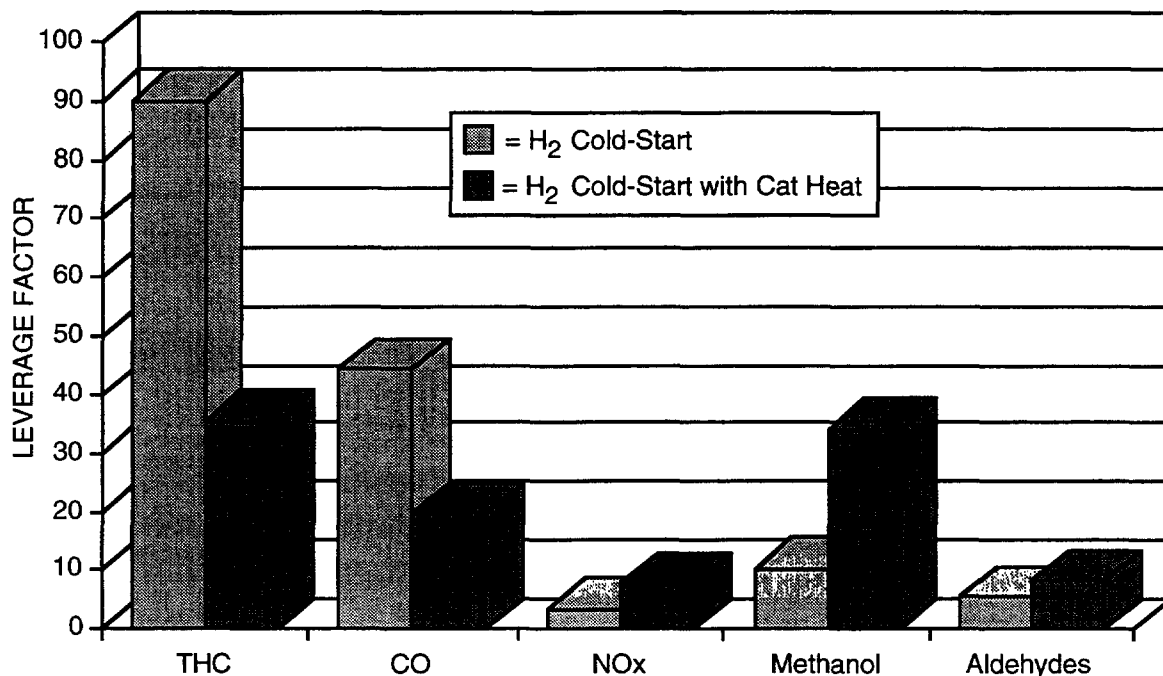


Figure 1-2: Leverage factors = % emission reduction ÷ % of fuel supplied as H<sub>2</sub>. Large leverage factors indicate highly effective use of hydrogen.

## 1.5 Hydrogen Generation

As an alternative to refueling a vehicle with its primary fuel plus hydrogen, hydrogen may be generated onboard in a number of ways. An electrolyzer could break down water with energy supplied from the vehicle's electrical system. Hydrogen may be separated from rich combustion products generated in one or more engine cylinders, recycling the balance to the intake air flow. Primary fuels may be partially oxidized, reformed, or cracked in onboard reactors.

The method selected for this project was onboard cracking of methanol. Section 8.0 is a bibliography that shows a rich background of previous work in this area. NREL's predecessor, the Solar Energy Research Institute (SERI), was among the leaders. The Colorado School of Mines (CSM) contributed to the SERI project. The collaboration of Dr. Scott Cowley of CSM was an invaluable asset in the present work.

The relatively small amount of hydrogen required to accomplish the emissions reductions described above scales the onboard cracker down to a much smaller size than required in the SERI vehicles. The rate of hydrogen production may be held constant as opposed to following the transient fuel demands of a motor vehicle. The cracking process can be carried out only when the temperature conditions are favorable for high hydrogen yields with minimized side reactions.

The present work was thought to be relatively insensitive to cracker product composition, as long as the hydrogen portion of the product can be efficiently separated and the products do not damage the separator. Neither of these assumptions turned out to be correct. Separation problems will be discussed below.

The other cracker products, along with slipped hydrogen from the separators, are fed to the engine as a supplemental fuel flow. The supplemental fuel flow is smaller than the engine's minimum fuel demand (idle). The engine controller simply decreases the primary fuel flow to compensate for the supplemental gaseous fuel. Figure 1-3 is a sketch of the system.

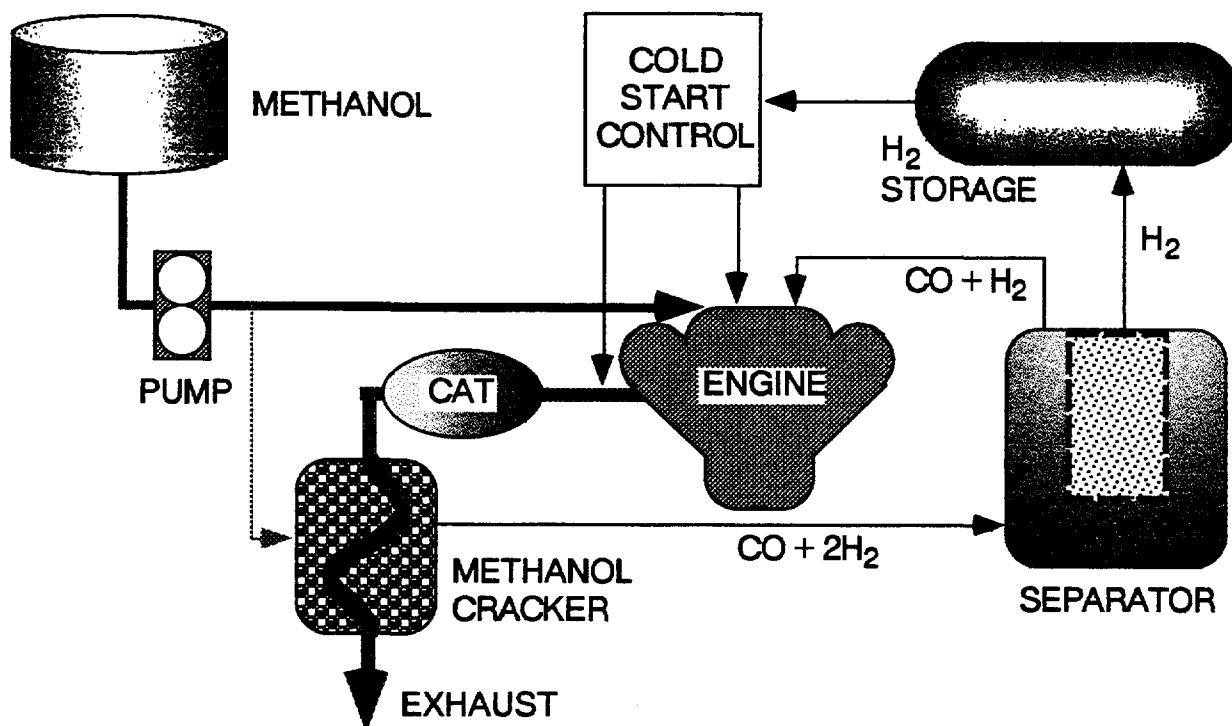


Figure 1-3: Diagram of hydrogen production and cold-start system.

Two methanol cracking catalysts were evaluated in bench testing. One was a commercial methanol synthesis catalyst supplied by United Catalysts, Inc., composed of copper and zinc oxides and alumina. This catalyst gave a high hydrogen yield (60+%), but after operation in the upper range of exhaust temperatures, it lost most of its activity. Subsequently, there was an objectionable rate of accumulation of methanol-rich condensate at the outlet.

A second catalyst, supplied by Dr. Scott Cowley of CSM, consisted of platinum and lanthanum oxide on alumina spheres. This catalyst was not damaged by heating to the upper range of exhaust temperatures. By retaining a high activity, condensate production was also much lower with the CSM catalyst.

In addition to the  $H_2$  and CO expected from an ideal decomposition of methanol, other species were observed. Several analytical methods were applied during the course of the bench and vehicle testing. HCl used thermal conductivity comparison, flame ionization, and infrared absorption (NDIR) instruments to study the cracker and separator products. CSM performed gas chromatography on gaseous product samples collected by HCl.

The products of methanol decomposition identified in this project over a range of temperatures typical of automobile exhaust included: hydrogen, carbon monoxide, carbon dioxide, methane, ethane, methanol, dimethyl ether, water, and carbon soot. A strong acid ( $pH < 2$ ) was generated at higher temperatures. No attempt was made to identify this product, although formic acid is the most likely candidate.

The CSM catalyst was loaded into the heat exchanger shown in Figure 1-4. HCl patterned the heat exchanger after a U-tube configuration developed in the earlier SERI project -- but of much smaller size. The heat exchanger is about the same size as the exhaust catalytic convertor on the Chevrolet Corsica test vehicle.

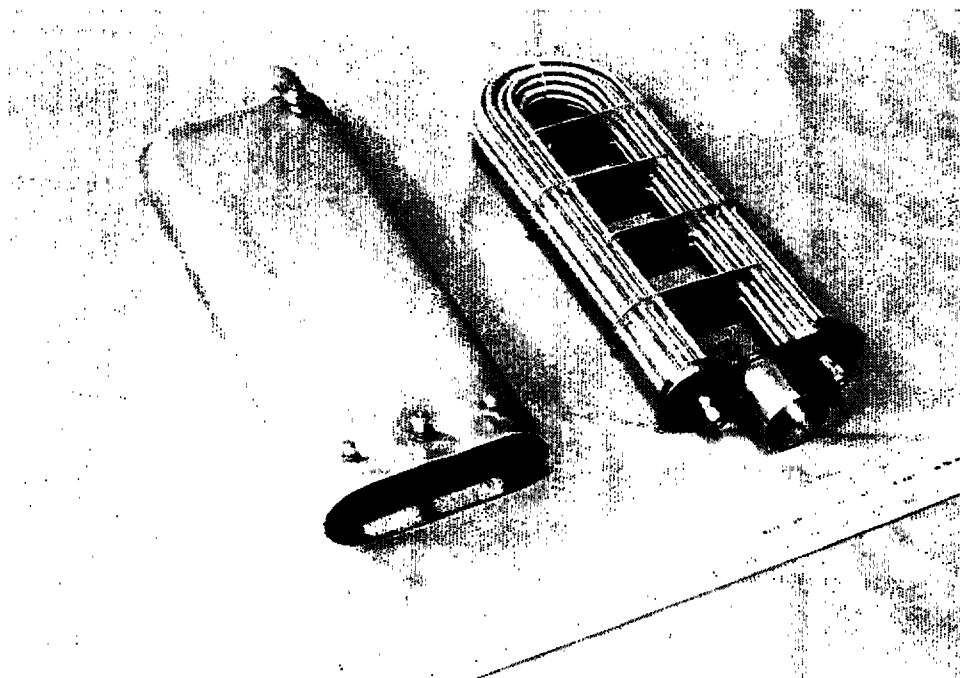


Figure 1-4: Photograph of the partially assembled reactor (scale units in inches).

## 1.6 Hydrogen Separation

Most hydrogen separation/purification processes commonly used in the chemical process industry are not well suited to onboard automotive applications. Two processes were seriously considered at the outset of this project: diffusion through palladium, and polymer membranes.

Diffusion through palladium is very specific to hydrogen because it involves migration of protons through the metal crystal lattice. Nothing else will fit. The problems with palladium separators are high cost, high temperature operation, vulnerability of thin tubes to sudden pressure changes, and the need to avoid pressure-temperature conditions that are conducive to the formation of palladium hydride. Hydriding the palladium tubes will cause cracking and leakage. There are palladium-silver alloys that are less prone to the hydriding problem, but the other shortcomings remain. HCl has worked successfully with palladium separators, but only in carefully controlled circumstances that are difficult to maintain in the automotive environment.

The alternative of polymer membranes was selected for evaluation in this project. The advantages are that the materials are not intrinsically expensive, the process works at room temperature, and the membranes are not fragile or prone to hydriding. Separation efficiency is very high for hydrogen/carbon monoxide; bench test experiments with binary  $H_2/CO$  mixtures went very well. First stage separation hydrogen content, at the flow required for the onboard application, was 91%. The second stage brought the hydrogen concentration to 99+%.

Separation difficulties began to surface during bench test experiments with actual methanol decomposition products. After initial vehicle reactor tests (when acidic condensates were noticed), the separator product contained  $CO$ ,  $CO_2$ , and methane. A high permeability for  $CO_2$  was expected from conversations with the separator manufacturer, but  $CO$  and methane slip was unexpected and unacceptable. Additional testing with the binary  $H_2/CO$  mixture still showed unacceptable separator performance with 5% $CO$  in the product. It's possible that the separator was damaged by alcohol, ether, or acidic condensates. Despite the use of a condensate trap during reactor testing, even pure hydrogen subsequently picked up enough organics through the separator to register 2500 ppmC on HCl's flame ionization detector.

## 1.7 Conclusions

The emissions test results with only 1%-2% of the vehicle's energy supplied as hydrogen showed highly leveraged improvements (emissions reductions much greater than the proportion of hydrogen burned). The hydrogen cold-start alone had the greatest leverage on total hydrocarbon and carbon monoxide emissions. The catalyst heating brought additional reductions in all pollutant categories, but the leverage was greater only for nitrogen oxides, methanol, and aldehyde emissions.

A practical advantage of cold-starting on hydrogen is that the vehicle always started immediately and idled smoothly. Federal emissions tests begin with the vehicle at room temperature. Starting reliability would be an even greater asset at outdoor winter temperatures where M85 starting is difficult and M100 starting is impossible. Hydrogen's gaseous state, high diffusion rate, and low ignition energy should all help to provide consistently easy starting.

Hydrogen was made onboard the test vehicle in a compact lightweight cracking reactor. The methanol cracking rate is limited by the need to consume the separator waste stream, even at an idling condition. However, so little hydrogen is needed that just 2 minutes of cracker/separator operation at temperature is needed to replenish the cold-start reservoir with only 50% of the cracked hydrogen recovered in the separator. The additional hydrogen needed for catalyst heating requires about 7 minutes of refill operation.

Temperature control of the reactor is necessary to get optimal hydrogen yields and avoid undesirable side reactions. This control was accomplished in HCl's chassis dynamometer testing by injecting a regulated flow of cool air into the exhaust stream. Over the range of vehicle operating conditions, the required air flow is 0% to 30% of the exhaust flow. Bypassing a portion of the exhaust flow is another possibility that was employed for temperature control in earlier work by SERI.

The membrane separator was effective at extracting hydrogen from mixtures of hydrogen and carbon monoxide, producing 99+% pure hydrogen. However, perhaps due to damage by strong acids and organic solvents generated in the cracker, it failed to produce the hydrogen purity required for the exhaust catalyst heating application. After exposure to actual cracker products, the permeate contained so much CO and THC that it could not be used in the vehicle tests. For simple cold-starting, a mixture of carbon monoxide, carbon dioxide, methane, and hydrogen should start much easier and produce less emissions than methanol during cold operation, so a separator would not be needed. Small methanol reformers for cold-starting have been previously demonstrated. However, the intent of this project was to demonstrate advanced hydrogen utilization by exploiting the unique clean burning and cold catalytic light off properties of hydrogen.

## 2.0 BACKGROUND

The Phase II work reported here is a continuation of the Phase I work that used minor amounts of hydrogen mixed with natural gas to get large emissions reductions. The results of the Phase I work are reported in National Renewable Energy Laboratory Report NREL/TP-425-6357. Achieving emissions reductions that are larger than the fraction of fuel energy supplied as hydrogen gives a form of *leverage* to justify the use of relatively expensive hydrogen with inexpensive natural gas. Phase II sought to achieve *leveraged* benefits with hydrogen produced onboard from methanol.

### 2.1 Hydrogen Cold-Start of a Natural Gas Vehicle

During the Phase I work, a different way of achieving *leverage* with hydrogen was proven. A test vehicle was operated on pure hydrogen during the first 505 seconds of the Federal Light-Duty Vehicle Emissions Test (i.e., a "Cold 505"). In addition to fueling the engine in an ultralean low NO<sub>x</sub> mode, a separate flow of hydrogen was delivered to the exhaust pipe where it burned with excess exhaust oxygen to heat the catalyst. The vehicle was operated in this mode for the first 20 seconds of the 505-second test. The balance of the test was completed with pure natural gas (6).

Surprisingly, hydrocarbon emissions went up by 20% during the hydrogen cold-start test. This is thought to be a test anomaly, perhaps caused by a gasoline canister purge during the hydrogen test (the vehicle runs on gasoline too). In any event, this vehicle has repeatedly shown non-methane hydrocarbon emissions well below the "ultralow emission vehicle" (ULEV) level in speciated tests by the California Air Resources Board. Hydrocarbon emissions are a non-issue with this vehicle when it is operated on natural gas.

The combined effect of burning hydrogen in the engine and the catalyst during the first 20 seconds of the test reduced CO emissions by 21% and NO<sub>x</sub> emissions by 33% relative to a baseline Cold 505 on natural gas alone. The fuel energy supplied as hydrogen was only 1.8%. Therefore, the *leverage* on CO was  $21\% \div 1.8\% = 12$ . The NO<sub>x</sub> *leverage* was  $33\% \div 1.8\% = 18$ . The results are presented graphically in Figure 2-1.

### 2.2 Hydrogen Cold-Start with Methanol

It is significant to note that these results were obtained with a vehicle whose cold-start emissions are very low, even without hydrogen. The test vehicle met California's ULEV emissions criteria in an extensive battery of tests. Cold-start emissions are a much larger problem with liquid-fueled vehicles. Although the hydrogen cold-start technique is also applicable to gasoline engines, it was decided to focus the Phase II work on methanol--partly because this is an *alternative* fuels project and partly because so much work had already been done by others in this area. A bibliography is presented in Section 8.0.

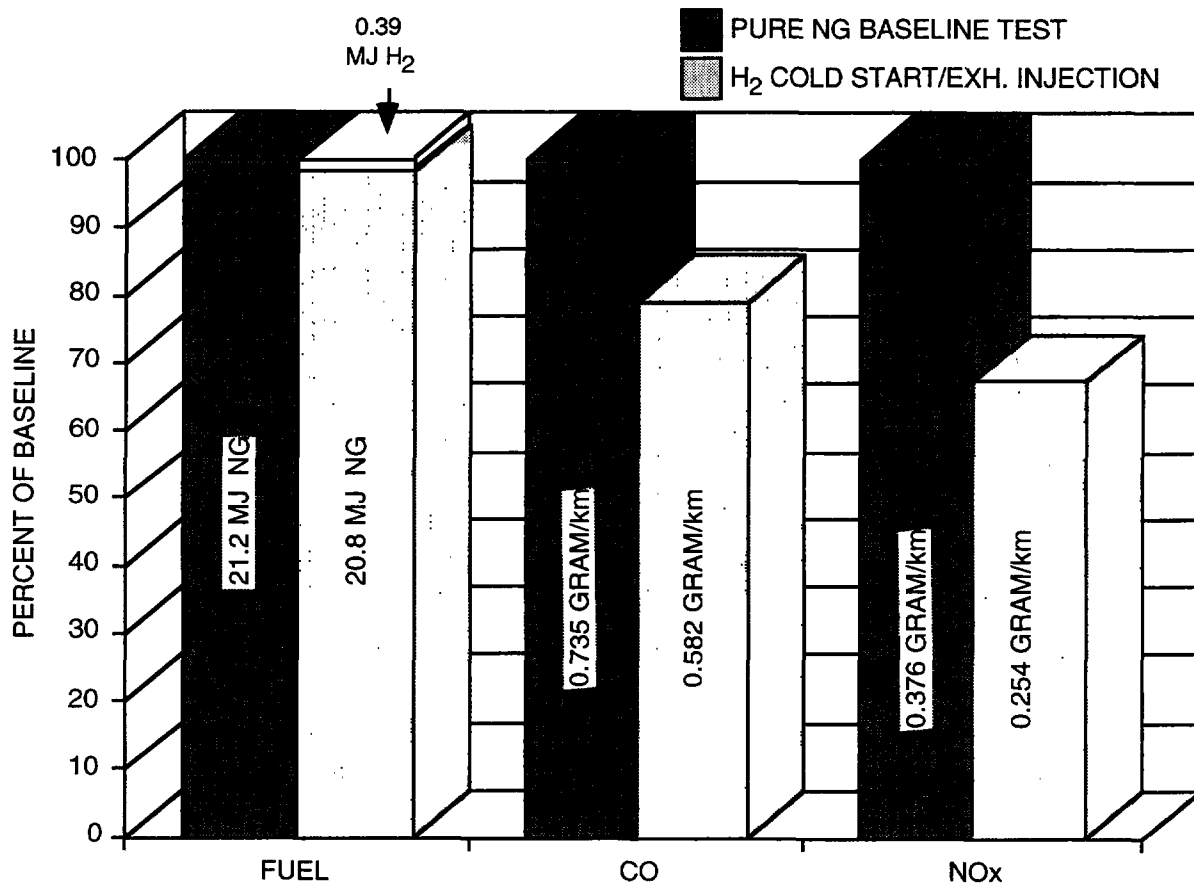


Figure 2-1: Comparison of two cold 505 tests: a natural gas baseline test, and a test with the first 20 seconds of operation on pure H<sub>2</sub> with H<sub>2</sub> injection into the exhaust to heat the catalyst.

It is clear from the literature that hydrogen-rich gaseous products can be obtained from the decomposition of methanol onboard a motor vehicle. It is also clear that cold-starting a vehicle with the gaseous products or with pure hydrogen separated from them will make significant reductions in emissions. The present work went forward from this rich background to explore advanced hydrogen separation technology and the effects of heating the catalyst with stored hydrogen.



### 3.0 CRACKER CHEMISTRY

Although methanol is the simplest of alcohols, its decomposition can be very complex. The desired dissociation reaction for the production of hydrogen simply yields hydrogen and carbon monoxide endothermically. The literature warns that actual decomposition produces many other products, depending on temperature and other factors. An exact knowledge of the product composition is unnecessary, given the approach shown in Figure 3-1.

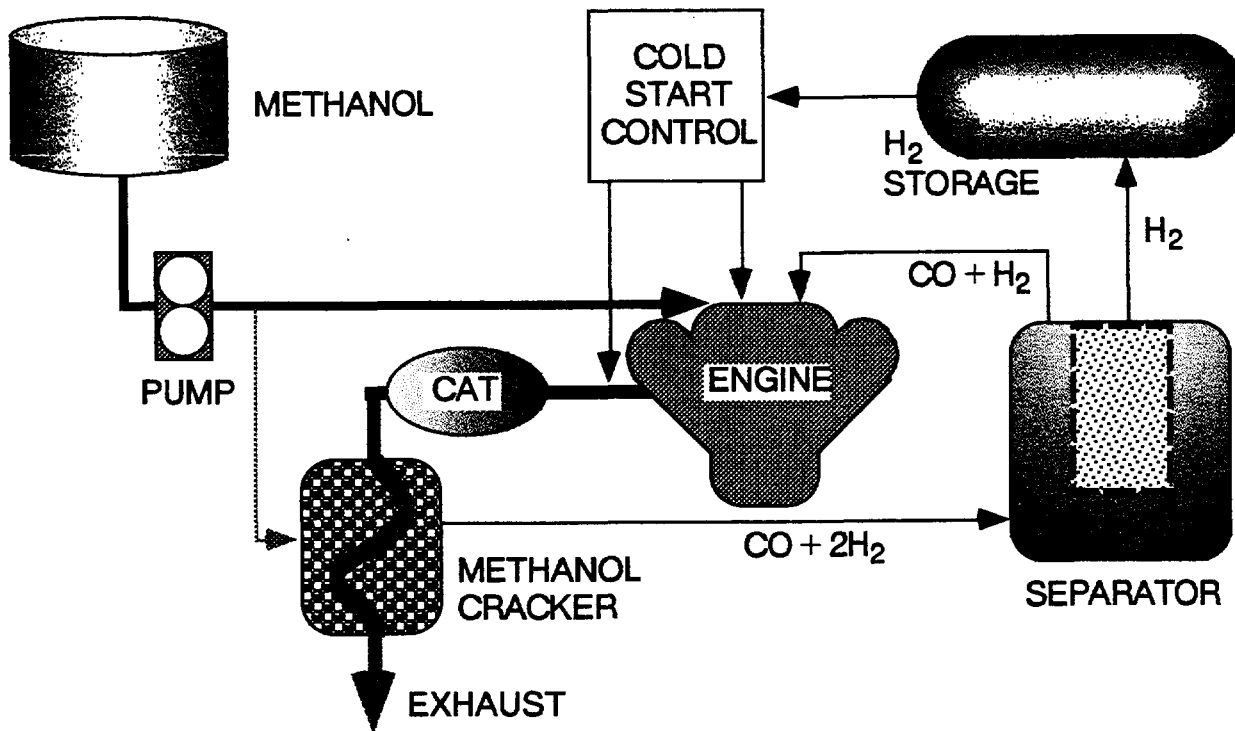


Figure 3-1: Diagram of hydrogen cold-start system.

The idea is to operate the engine on methanol, except during cold-starts. A much smaller flow of methanol is cracked and separated. The hydrogen portion of the cracked product is stored for future cold-starting. The balance of the cracked product is bled to the engine at a rate that is well below the minimum fuel demand of the engine. The engine fuel controller simply decreases the main fuel supply slightly to accommodate the supplemental fuel. The process is quite simple if the separator is highly effective at isolating hydrogen from the myriad of possible products.

At low temperatures, equilibrium favors exothermic dehydration which produces water and dimethyl ether. At higher temperatures, exothermic formation of methane and water from methanol and hydrogen is favored. Equilibrium also favors carbon soot and carbon dioxide formation from carbon monoxide over a wide temperature range (9, 10). The products from the unwanted reactions are involved in side reactions as well; Table 3-1 lists some of the possible results.

Table 3-1: Decomposition and Side Reactions of Methanol

Reaction	kcal/mole
$\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$	21.66
$2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	-2.97
$\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$	20.38
$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$	11.83
$\text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-27.61
$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{HCO}_2\text{CH}_3$	-10.19
$\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2$	48.03
$\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2$	-0.11
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-45.87
$\text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	-0.10
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-9.83
$2\text{CO} \rightarrow \text{C} + \text{CO}_2$	-41.21

Expected products include: hydrogen, carbon monoxide, carbon dioxide, dimethyl ether, methane, water, acetic acid, formaldehyde, and carbon soot. Also, there are possible side reactions involving hydrogen peroxide, formic acid, performic acid, and the synthesis of ethane, ethylene, and propane (22, 24, 23, 18, 2).

During reactor and catalyst development, product samples were taken for gas chromatographic (GC) analysis. The actual products observed included hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and traces of dimethyl ether. By balancing the relative proportions of these products against methanol, additional dimethyl ether and water (which were removed from the product stream as condensate) can also be inferred from stoichiometry. At lower temperatures, the condensate had an etheric smell. At higher temperatures, a very acidic condensate was produced from which acetic acid or formic acid production can also be inferred.

## 4.0 EXPERIMENTAL SETUPS

### 4.1 Test Vehicle Description

The vehicle used for this project was a 1988 Chevrolet Corsica, which was the student entry from Colorado State University in the 1989 DOE/SAE Methanol Marathon competition. The vehicle specifications are listed in table 4-1.

Table 4-1: Test Vehicle Description

#### 1988 Cheverolet Corsica

Engine Type	2.8 liter, 60° V6 Custom pistons for 12:1 compression ratio
Drive Train	5-speed manual transaxle, front wheel drive
Emission Controls	Exhaust gas recycle (EGR) Stock gasoline three-way catalytic convertor Oxygen sensor feedback Evaporative emission canister
Methanol Modifications	Methanol-compatible components: Stainless-steel fuel tank and lines Methanol-tolerant fuel pump Anodized fuel rails Larger, methanol-tolerant injectors Programmable electronic control module
Hydrogen Modifications	Precision orifice hydrogen distribution block Hydrogen injection ports installed in intake manifold Hydrogen injection tube in exhaust (Fig. 4-1) Thermocouples in exhaust and catalytic convertor Injector disable switch

With the programmable electronic control module (ECM), the fuel tables could be modified for operation on different fuels, such as M85 (a mixture of 85% methanol, 15% gasoline by volume) or M100 (pure methanol). For hydrogen cold-starting, a switch was installed on the injector power supply to disable methanol operation. The hydrogen flow was controlled through a pressure regulator and metering valves to the hydrogen distribution block on the engine and the exhaust injection tube. A thermal mass flow meter on the hydrogen line ensured consistent start-ups. With the ultra-lean hydrogen cold-starting mixture, extra air is required to idle the engine at a normal speed. The hydrogen flow was carefully controlled to maintain an idling speed slightly below the ECM's normal idle air control speed. In this way, the idle air controller was always wide open during hydrogen operation, and the idle speed remained stable.

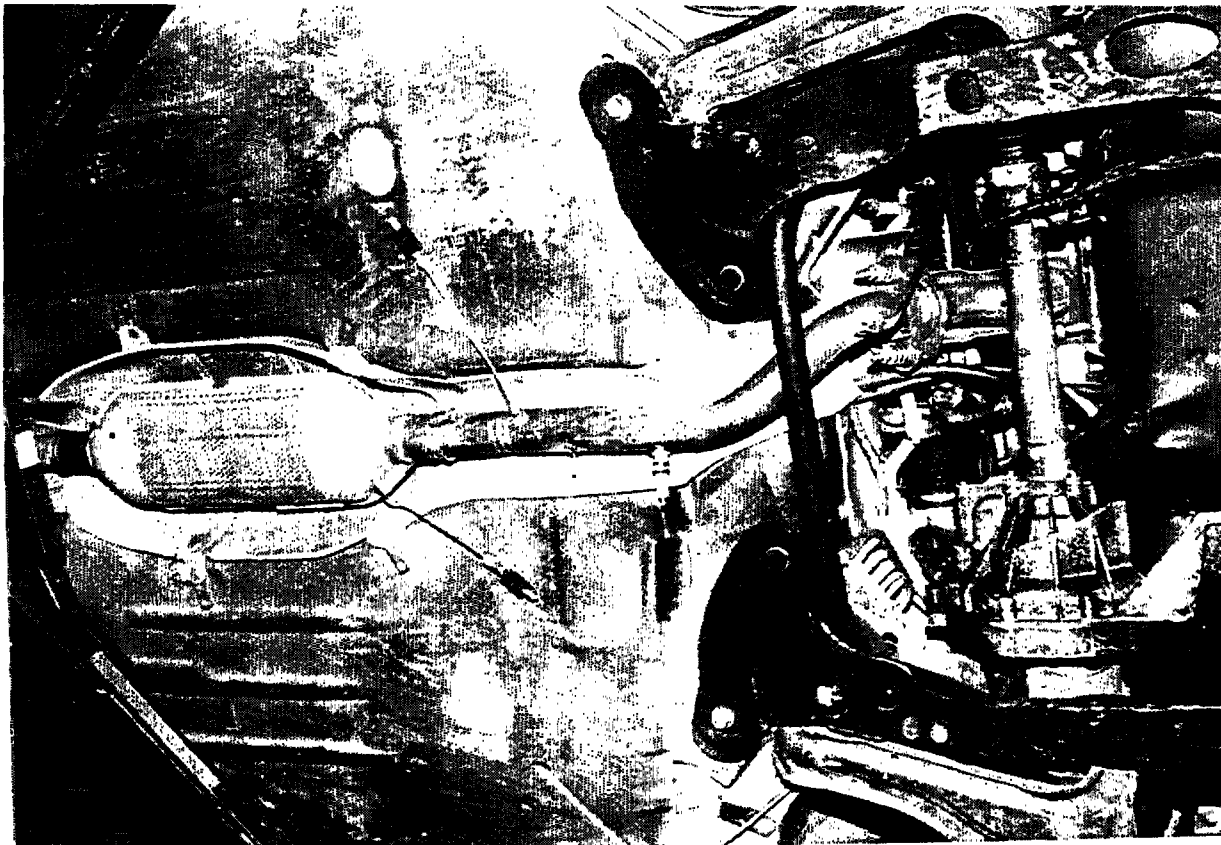


Figure 4-1: Exhaust and catalytic convertor modifications. The hydrogen injection tube can be seen just after the coupling to the down-pipe. Thermocouples were installed upstream and on the surface of the catalytic convertor.

## 4.2 Bench Test Cracker and Separator System

### Reactor:

To evaluate different dissociation catalysts, a bench-top reactor system was built to test a small catalyst sample at conditions expected in the vehicle (see figure 4-2). A methanol pump with adjustable flow rates provides the high pressure needed for the separation process. A vaporizer tube feeds methanol down to the bottom of the vertical furnace and into a high pressure reactor. The reactor itself is simply a 0.5 inch OD x 0.035 inch wall thickness x 5 inch long, 316 stainless-steel tube filled with the catalyst. Stainless-steel filters at each end of the tube retain the catalyst. This up-flow arrangement was chosen to prevent the flow from packing the catalyst and also to maximize methanol contact with the catalyst. A coaxial, counterflow heat exchanger is installed between the methanol flow in and the product flow out. The products then travel through a high pressure condensate trap and coalescing filter. Back-pressure regulators maintain high pressure in the reactor and separation systems, and thermocouples are installed on the reactor tube and inside the furnace around the reactor.

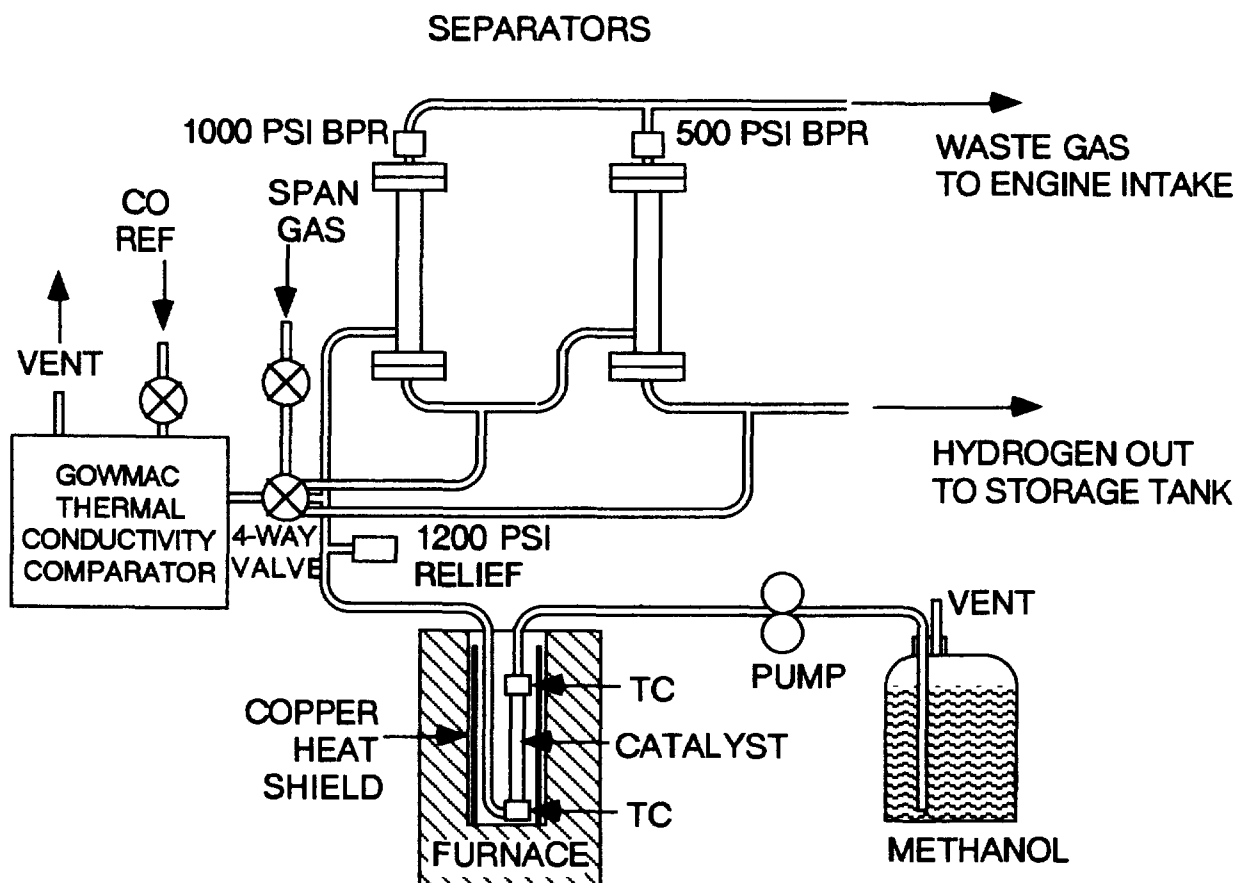


Figure 4-2: Bench top catalyst testing system.

#### Thermal conductivity sampling:

Samples could be taken from the reactor or any of the separation stages for thermal conductivity measurement of hydrogen concentration. A thermal conductivity comparator (GOW-MAC model 20-260; see reference 8) was calibrated with six prepared  $H_2/CO$  mixtures. Two tanks with equal volumes were evacuated and filled with either hydrogen or carbon monoxide at known pressure in a temperature-controlled laboratory. From NIST data tables, the exact quantity of each gas in each tank could then be calculated. The two tanks were connected, and the gases were allowed to mix. While the mixtures were sampled, the two tank valves were shut one after the other. Any variation in thermal conductivity reading indicated that the mixing time was insufficient, and the experiment would be repeated. These calibration gases produced the response curve shown in Figure 4-3. Although methanol decomposition produces many different gases, their thermal conductivities are all small compared to hydrogen (see Table 4-II). Samples were also taken for gas chromatography analysis by Dr. Scott Cowley at the Colorado School of Mines.

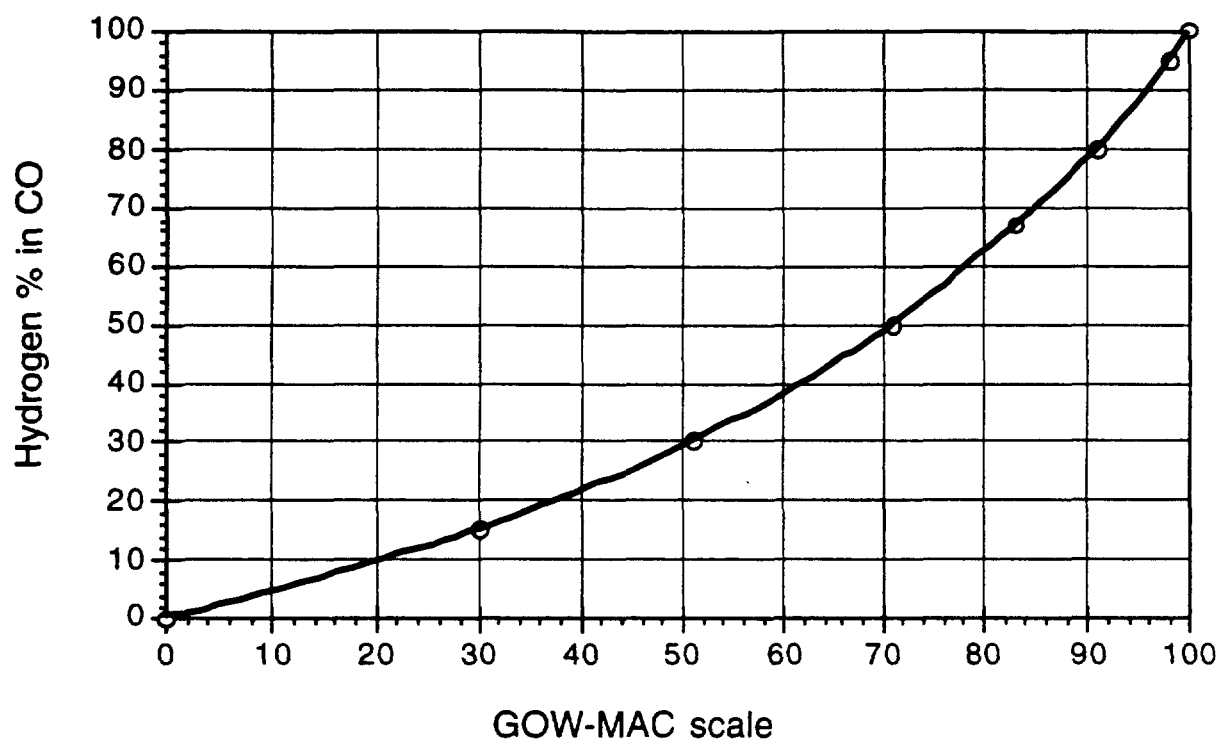


Figure 4-3: Response calibration of thermal conductivity hydrogen analyzer.

Table 4-II: Thermal Conductivities of Methanol Decomposition Products (8)

Component	Thermal Conductivity (Air = 1)
Methanol vapor	0.547
Carbon monoxide	0.964
Carbon dioxide	0.636
Water vapor	0.692
Methane	1.312
Ethane	0.834
Ethylene	0.780
Propane	0.700
Ethyl ether	0.579
<b>Hydrogen</b>	<b>6.943</b>

#### Hydrogen Separators:

Several hydrogen separation alternatives were considered early in the project. Hydrogen can diffuse through palladium at temperatures above 300°C (19, 20, 16, 12, 3). However, palladium is expensive and will form hydrides and crumble if the hydrogen is not purged as it cools. Palladium separators are commercially available, but the thin delicate tubes and precise thermal and purge control requirements were judged incompatible with an automotive environment.

## PRISM® Separators:

The polymer membrane is actually a bundle of hollow fibers potted together in a shallow plastic cylinder on one end and sealed on the other end. The feed gases flow around and through the bundle on their way out of the shell through the back-pressure regulator. The potted end forms a tube sheet which is sealed from the feed flow and held at a lower pressure. This pressure differential forces gases from the outside (feed side) of the fibers to the inside (permeate side). Certain gases ( $H_2$ ) permeate through the fibers faster than others (CO); so as long as there are flows on both sides of the fibers, the gases can be separated.

The two-stage membrane separator system was designed by PERMEA, Inc.<sup>1</sup> with the following specifications:

STREAM COMPONENT		Feed	Non-Perm1	Permeate1	Non-Perm2	Permeate2
$H_2$	mol%	66.67	36.43	92.30	77.50	98.57
CO	mol%	33.33	63.57	7.70	22.50	1.43
FLOW	slm <sup>2</sup>	27.78	12.74	15.03	4.48	10.56
PRESS	psia	633.00	623.00	300.00	290.00	215.00

These separators are normally used in large petrochemical plants, so the fiber bundles were installed in large, heavy shells with extremely large high-pressure flanges. The actual bundle size, however, is approximately 1 inch diameter by 12 inches long (see Figure 4-4--picture of bundle). With high pressure tubing and compression fittings rather than flanges, the separator system (with back-pressure regulators) could fit in a 1/2 ft<sup>3</sup> volume.

For two-stage separation, the permeate from the first stage becomes the feed for the second stage. Because the permeate quality improves with increasing membrane differential pressure, the first stage was maintained at 750 psig, the second stage at 375 psig, and the second stage permeate pressure varied with storage tank pressure during testing. Back-pressure regulators hold the required pressures on the first and second separation stages, while a relief valve controls a maximum storage tank pressure of 250 psig. The 10 slm<sup>3</sup> permeate flow was chosen to quickly refill the 50 standard liters of hydrogen used during the cold-start. This refill time must not be too fast, however, because the engine must be able to consume the total non-permeate waste stream, even during idle conditions. The feed rates are adjustable with the variable-displacement high-pressure methanol pump.

<sup>1</sup> A division of Air Products and Chemicals, Inc. Air Products cost-shared in the purchase of the separators.

<sup>2</sup> Standard liters per minute; standard conditions are 0°C, 101kPa.

<sup>3</sup> Standard liters per minute; standard conditions are 0°C, 101kPa.

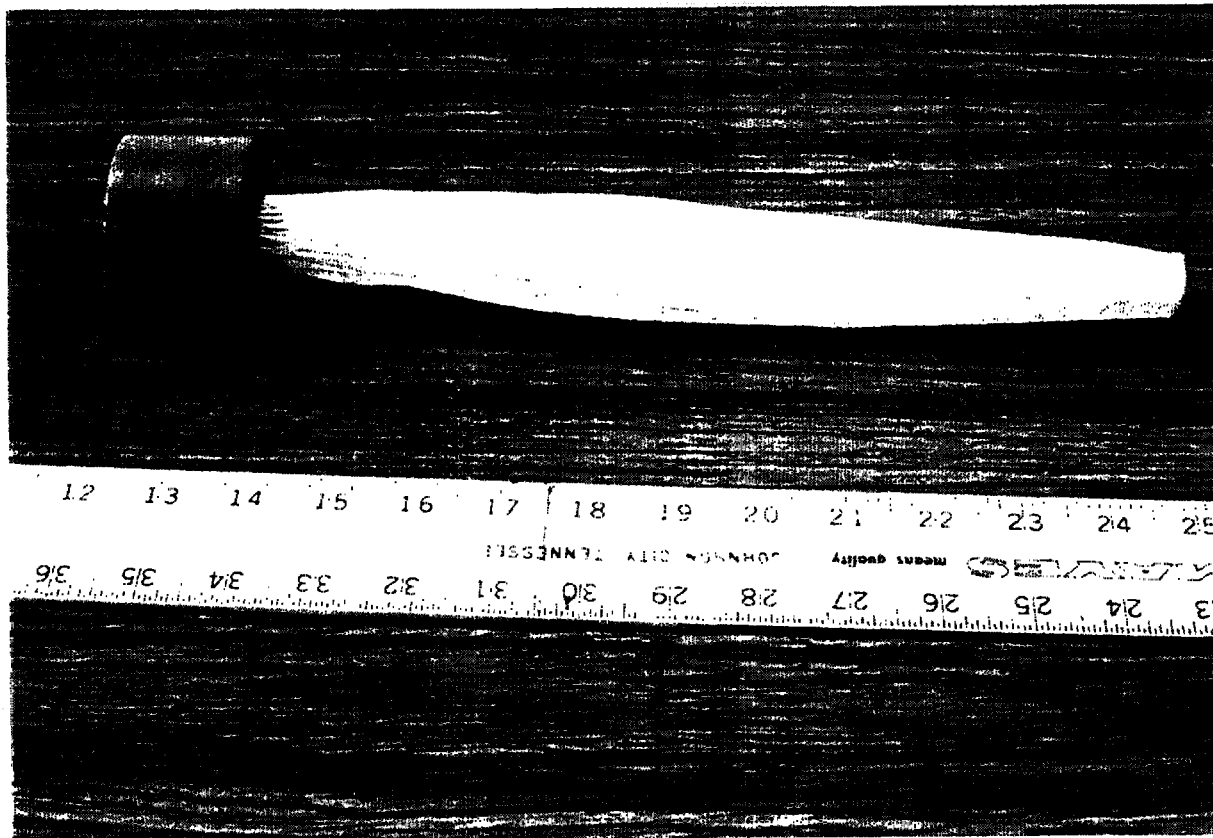


Figure 4-4: Photograph of hydrogen separator bundle (scale units in inches).

### 4.3 Catalyst Selection

There are many criteria and associated tradeoffs with the selection of a methanol decomposition catalyst. Because the goal is to produce and store hydrogen, the dissociation reaction to CO and H<sub>2</sub> is the most desirable. Therefore, the catalyst must be selective for dissociation or inhibit other possible reactions and side reactions. The catalyst must also be active enough to decompose methanol at a rate which will refill the hydrogen storage tanks in a reasonable time with a reasonable reactor size and weight. This level of activity should be present within a normal vehicle exhaust temperature range. However, the catalyst must not be deactivated by high temperature excursions. Finally, the catalyst must be mechanically strong enough to endure temperature cycling, the expansion and contraction of the reactor, and engine and vehicle vibration (22).

Because dissociation is the inverse of commercial methanol synthesis, the same catalysts can be used. These catalysts are usually based on combinations of common metal oxides, such as copper, zinc, nickel, and chromium. These catalysts have excellent activity and selectivity at relatively low, controlled temperatures. However, during high temperature excursions, the formation of carbon soot deactivates the catalytic surfaces. The mechanical strengths of these catalysts are also usually not good; crumbled catalyst particles can clog the reactor outlet filter (5, 14, 23, 17, 11, 2).



Noble metal catalysts such as platinum and palladium have also come of interest for automotive methanol reformers because of their high-temperature durability and long life. However, the substrate on which the catalyst is deposited can affect the selectivity. Acidic sites on  $\gamma$ -alumina promote methanol dehydration to dimethyl ether and water. Suitable modifiers such as lanthanum and potassium can reduce these tendencies (23, 21, 22, 14, 18).

#### 4.4 Onboard Heat Exchanger/Decomposition Reactor

The previous experience of SERI/NREL and Dr. Scott Cowley of CSM was invaluable in the design of the reactor (5, 14). The first SERI vehicle reactor used straight tubes full of catalyst between two tube sheets. The sudden temperature change during vehicle start-up produced different expansion rates in the tubes; the reactor began leaking when the tubes buckled and broke the seal at the tube sheet. The use of a U-tube design solves the expansion problem, and this tube configuration was adopted in the HCI design. The location of the decomposition reactor between the catalytic converter and the muffler requires a low profile under the vehicle, while the separation process requires high-pressure capability. A photo and diagram of the reactor are shown in Figures 4-5 and 4-6. Table 4-III lists the specifications of the final reactor design.

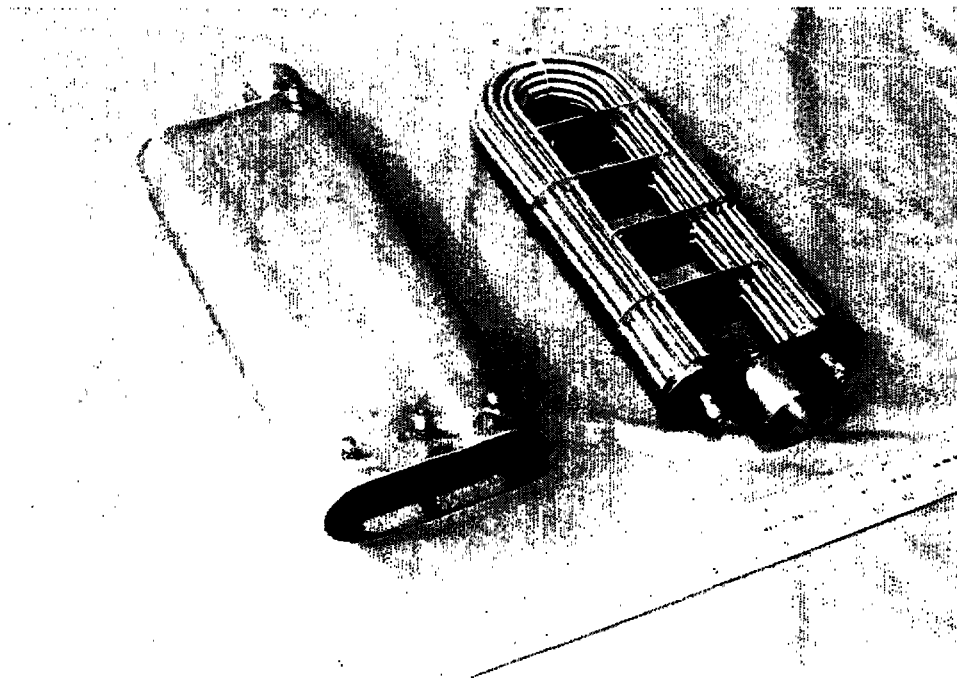


Figure 4-5: Photograph of the partially assembled reactor (scale units in inches).

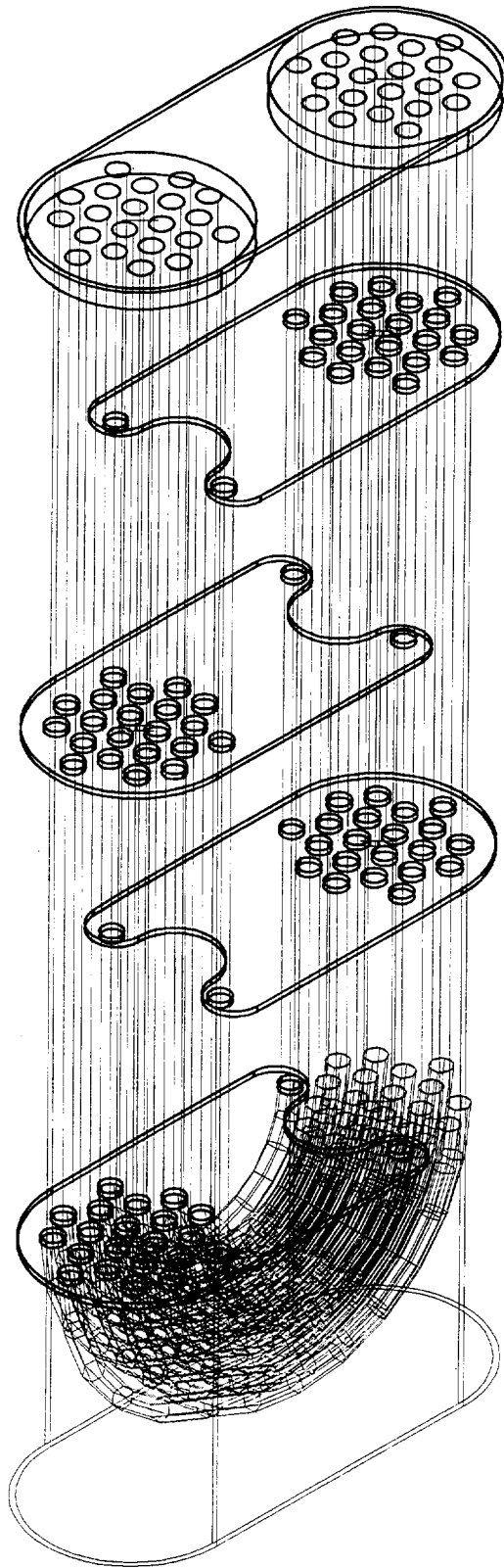


Figure 4-6: Diagram of vehicle reactor design.

Table 4-III: Reactor Specifications

**HCl Methanol Dissociation Reactor**

Material	316 stainless steel, 304 stainless steel (shell)
Configuration	Shell-and-tube, 21 U-tubes, 5 pass on shell side, 2 pass on tube side
Shell-side fluid	Exhaust gas
Tube-side fluid	Methanol and dissociation products over catalyst
Tube dimensions	6.35mm (0.25 inch) OD x 0.7112mm (0.028 inch) wall
Tube volume	350 cm <sup>3</sup> (21.36 in <sup>3</sup> )
Tube surface area	0.3437 m <sup>2</sup> (3.7 ft <sup>2</sup> )
Overall dimensions	43.18 x 17.78 x 7.62 cm (17 x 7 x 3 inches)
Total Weight	5.45 kg (12 pounds)
Total Catalyst Weight	245 g (0.54 pounds)



## 5.0 TEST RESULTS

### 5.1 Catalyst #1

Early in the project, methanol decomposition was discussed with commercial catalyst manufacturers. United Catalysts, Inc., provided samples of a copper oxide and zinc oxide methanol synthesis catalyst for evaluation. The specifications of this catalyst are shown in Table 5-1.

Table 5-1: Catalyst#1 Specifications

**United Catalysts, Inc., Methanol Synthesis Catalyst Type L-951**

Composition	67%CuO, 22%ZnO, 11%Al <sub>2</sub> O <sub>3</sub>
Surface Area	50-90 m <sup>2</sup> /g (6.35 mm diameter x 3.175 mm tablets)
Pore Volume	0.25-0.35 cm <sup>3</sup> /g (6.35 mm diameter x 3.175 mm tablets)
Form and Size	Tablets ground and sifted to -50+100 mesh powder

#### Bench Tests:

The copper oxide catalyst was ground to increase the surface area and provide better loading for methanol contact in the small bench top reactor. The reactor was loaded with 7.7 g of catalyst. To avoid damaging the separators with unknown products, the first tests ran directly through the first stage back-pressure regulator rather than through the separators. The methanol pump was varied between 2.5 and 6 hr<sup>-1</sup> WHSV (Weight Hourly Space Velocity = g/hr methanol ÷ g catalyst), and the reactor pressure was held at 900 psig to simulate anticipated separator conditions for all tests.

The initial test at 350°C demonstrated very high dissociation selectivity with a hydrogen concentration of 64% in the product. The maximum possible hydrogen concentration is 66.7%; any other decomposition or side reactions would lower the hydrogen yield (except carbon soot formation, which would increase the hydrogen concentration). During testing at 450°C, the hydrogen concentration remained very high at 64%, but unreacted methanol began to flood the condensate trap and plumbing. This deactivation at higher temperatures is caused by carbon soot and carbon dioxide formation from carbon monoxide, when the solid carbon coats and clogs the catalytic surfaces (21, 22, 23). This reaction should have increased the hydrogen concentration reading, but other side reactions may have balanced this effect. Subsequent tests were performed at lower temperatures to a minimum of 250°C. Hydrogen concentration always remained above 60%, but the initial activity was never recovered, and condensate continued to flood the system plumbing. This high temperature deactivation was judged to be incompatible with an exhaust-heated reactor.

## 5.2 Catalyst #2

After reviewing the literature for other possible catalysts, Dr. Scott Cowley of the School of Mines was consulted. Dr. Cowley has more than ten years' experience with alcohol decomposition catalysis, including the SERI/NREL dissociated methanol Ford Escort. Previous work with platinum- and palladium-based catalysts demonstrated much better high temperature activity and stability than the copper oxide materials. Although palladium has slightly better activity, the better durability of platinum was chosen to ensure success over a wide temperature range. A platinum catalyst with a lanthanum oxide modified alumina substrate was prepared by Dr. Cowley for evaluation. The specifications for this catalyst are shown in Table 5-II.

Table 5-II: Catalyst#2 Specifications

**CSM Methanol Dissociation Catalyst**

Composition	2%Pt, 5%La <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub>
Support	Norton SA-6373 g-alumina 1/16 inch spheres
Packing Density	Approx. 0.7 g/cm <sup>3</sup>
BET Surface Area	200-240 m <sup>2</sup> /g
Pore Volume	0.57-0.67 cm <sup>3</sup> /g

### Bench Tests:

The bench top reactor was loaded with 5.3 g of catalyst. The methanol pump was set to provide 3 - 4 hr<sup>-1</sup> WHSV, based on Dr. Cowley's work with this catalyst. Reactor pressure was held at 900 psig to simulate anticipated separator conditions for all bench testing. The products of the first test at 375°C showed a hydrogen concentration of 58%. This concentration remained constant up to 450°C, where the reactor temperature suddenly increased to 490°C. Although the furnace setting was decreased to 400°C, the reactor remained at 460°C for several hours until the methanol flow was turned off. This operating condition is thought to be a balance between endothermic dissociation, which produces hydrogen, and the exothermic reaction of methanol and hydrogen to produce methane and water. During this time, the thermal conductivity instrument showed 24% - 40% of the self-heating product was hydrogen; but a sample taken for GC analysis shows the composition in Table 5-III when balanced stoichiometrically with methanol.

Table 5-III: Self-Heating Methanol Decomposition Product

Component	Mole%
CO	6.17
CH <sub>4</sub>	21.75
CO <sub>2</sub>	18.14
C <sub>2</sub> H <sub>6</sub>	2.69
H <sub>2</sub> O	9.00
H <sub>2</sub>	42.25

The net heat of reaction for the above self-heating products is exothermic at about -6 kcal/mol methanol. The relative concentrations of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in these self-heating products indicate that an appreciable amount of the methanol and methane steam reformation and water-gas shift reactions were occurring. From a hydrogen production viewpoint, these reactions are helping to recover some of the losses from the methanation reaction.

After the methanol flow was shut off, the reactor was cooled to  $390^\circ\text{C}$ , and the methanol flow resumed. The product hydrogen went back up to 60% immediately and remained above 58% as the reactor was cooled to a minimum of  $325^\circ\text{C}$ . Throughout all bench testing with this catalyst, the condensate production rate was very low. The minimal condensate that was recovered seemed to be water gravimetrically, but with an etheric smell. The fact that unreacted methanol was not observed by density measurements or smell indicates very good activity for this catalyst at modest space velocities.

#### Vehicle Reactor Tests:

With the success of the bench tests, this catalyst was chosen for the full-size onboard reactor. The catalyst was produced by Dr. Scott Cowley of CSM. The specifications of the heat exchanger/reactor, fabricated at HCl, are listed in Table 4-III and a photo of the installed reactor is shown in Figure 5-1.

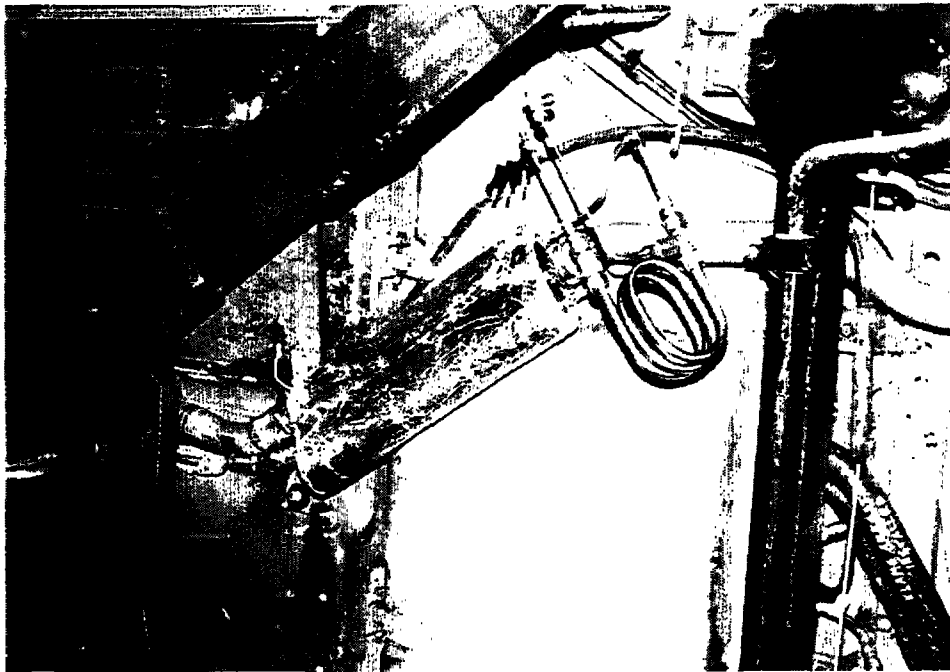


Figure 5-1: Methanol decomposition reactor installed in vehicle.

The reactor was fitted with thermocouples at the exhaust inlet (at the bend in the U-tubes), at the exhaust outlet, and in the tube bundle behind the tube sheets at the reactor inlet and outlet. These locations were chosen to represent the widest temperature differentials of the system. Testing of the vehicle reactor was performed on a chassis dynamometer at HCl. The methanol pump, separator system, and thermal conductivity sampling system was the same as for the bench tests. The methanol pump was set to produce 12 cc/min of methanol = 2.33 hr<sup>-1</sup> WHSV which would provide a dissociated product flow of 20 slm. With an anticipated separator hydrogen recovery of 50%, the hydrogen storage tank refill would take about 6 minutes. The temperature of the reactor was controlled by operating the vehicle at different power levels, running on M100 plus the separator waste stream. The test conditions and GC analysis of the first test are given in Table 5-IV.

Table 5-IV: Test#1 Conditions and Products

TEMPERATURES	°C	PRODUCTS	mol%
Methanol in	328	CO	8.25
Products out	383	CH <sub>4</sub>	25.77
Exhaust in	399	CO <sub>2</sub>	16.49
Exhaust out	354	CH <sub>3</sub> OCH <sub>3</sub>	0
		H <sub>2</sub> O	9.28
		H <sub>2</sub>	40.21

This test condition had products similar to the self-heating bench reactor experiment, but at lower temperatures. Most notable from this test was the production of a very acidic blue-green condensate. The density of the condensate was very close to water, and a test with litmus paper showed a pH < 2. Acetic acid is one possible component for this product, but the condensate did not have its familiar vinegar smell. In any case, the acid is too strong for acetic acid to be the only acidic component. The current hypothesis is that formic acid was produced, which would imply that the acid would have a concentration greater than 0.55M to get below than pH 2. It is also puzzling that this acid was not observed during bench testing or during previous testing by Dr. Cowley. To reduce the methanation reaction, the next test was performed at lower temperatures. Table 5-V lists the test conditions and GC analysis results.

Table 5-V: Test#2 Conditions and Products

TEMPERATURES	°C	PRODUCTS	mol%
Methanol in	284	CO	20.79
Products out	316	CH <sub>4</sub>	5.94
Exhaust in	350	CO <sub>2</sub>	7.92
Exhaust out	296	CH <sub>3</sub> OCH <sub>3</sub>	3.96
		H <sub>2</sub> O	1.98
		H <sub>2</sub>	59.41

The hydrogen production at these lower temperatures was much better, and in general the dissociation reaction is dominant. The light brown condensate from this



test also had the density of water. However, it was not acidic and smelled etheric like the bench reactor condensate. The GC analysis showed lower dimethyl ether and water concentrations than table 5-V, but these numbers had to be higher to balance stoichiometrically with methanol. This supports the hypothesis that some of the dimethyl ether condenses in solution with the water.

Because of the poor hydrogen yield, exothermic reactions, and acid production at higher temperatures, it was clear that during actual emissions testing the exhaust temperature would have to be controlled. In the SERI vehicles, bypass valves were installed to route the exhaust either through or around the decomposition reactor. However, because of reported trouble with these valves and the added plumbing complexity, a different strategy was implemented. In the next series of separator tests, which are reported below, compressed shop air was injected into the exhaust just before the reactor, using a solenoid controlled by the data acquisition computer. This method was successful at controlling the reactor temperature and could be accomplished with an automotive air injection (smog) pump.

### 5.3 Separator Performance

To evaluate the separator system performance, a gas mixture of 60% H<sub>2</sub> and 40%CO was prepared by partial pressures and checked with the thermal conductivity instrument. This mixture was then fed through the separators at a controlled flow to produce 5-6 slm of final permeate flow. The first stage feed was set to 750 psig, and the permeate (which becomes the feed for the second stage) was set to 375 psig. The hydrogen enrichment at this point in the system was 91% H<sub>2</sub>. The final, second stage permeate was set to 250 psig, and the final hydrogen concentration was over 99% H<sub>2</sub>. With these positive results, the system was installed on the vehicle reactor system for actual decomposed methanol testing.

After the first two vehicle reactor tests (reported in section 5.2), further tests were run with average reactor temperatures over the 370°C-290°C range with the separators on-line. It was noticed that the separator product hydrogen was reading fairly low, so these gases were checked through HCl's exhaust emission bench which included an infrared Horiba CO/CO<sub>2</sub> analyzer and a Beckman Flame Ionization Detector (FID). These separator products were fairly consistent, with 77% H<sub>2</sub>, 15% CO<sub>2</sub>, 5%CO, and at least 1% CH<sub>4</sub> (the FID can only read up to 10,000 ppm). To check the separators, the 60/40 test gas was run through the separators again. This test showed 95% H<sub>2</sub> and 5%CO, down from the 99+% H<sub>2</sub> in initial testing. The test mixture picked up enough organics through the separators to register 2500 ppmC on the FID.

A discussion with PERMEA revealed that fairly high CO<sub>2</sub> slip was to be expected, but there should not have been the CO and, especially, the CH<sub>4</sub> slip. At higher reactor temperatures, the acidic condensates were still being formed, and some of these products were found downstream of the coalescing filter/condensate trap. PERMEA also stated that acidic or methanol condensates could strip the coatings off the separator fibers and degrade the performance.<sup>1</sup> For an engine cold-start fuel, this degraded separator performance would be tolerable, but during exhaust injection the CO and CH<sub>4</sub> would slip right through a cold catalytic convertor.

#### 5.4 Vehicle Baseline Tests

All the vehicle emissions testing was performed at the National Center for Vehicle Emission Control and Safety (NCVECS) on the Colorado State University campus. With the addition of a Nicolet REGA 7000 Fourier Transform Infrared (FTIR) system from the Engines and Energy Conversion Laboratory at CSU, time-resolved, speciated emissions measurements from the constant volume sampler (CVS) could be performed during the Federal Test cycle. Total methanol, aldehyde, and speciated hydrocarbon mass emissions can then be integrated from the FTIR modal concentrations and the total CVS volume for the test cycle.

The FTIR instrument was factory calibrated for natural gas testing. This analytic method was modified to include methanol and aldehydes. To verify this method, typical emission span gases (CO, CO<sub>2</sub>, NO<sub>x</sub>, C<sub>2</sub>H<sub>6</sub>) from NCVECS were tested, along with a methanol standard span gas provided by the Colorado Department of Health. In addition, "recoveries" were performed with methanol and paraformaldehyde. A recovery test involves injecting a known quantity of the substance to be measured directly into the CVS test pipe. The FTIR concentrations can then be integrated to see if the total measured mass matches the known injection mass. Because this technique approximates the actual conditions of a federal test, it is a very powerful evaluation of the entire analysis system. The methanol recoveries were excellent, with less than 2% error over a 505 second injection time. The recovery of formaldehyde was also very good, with less than 3% error over 505 seconds.

One of the goals of the project was to provide a reliable cold-start with a methanol fueled vehicle. Because methanol is difficult to cold-start, this could cause significant difficulty and variability in the baseline emission tests (4, 7, 1, 13, 15). For these reasons, the baseline tests were performed with M85, which does reliably start at room temperature. The ECM fuel tables were reprogrammed for operation on M85, but the cranking and cold engine enrichment tables were left with stock gasoline values. All other ECM functions (e.g., EGR, ignition timing) were also left with stock gasoline values to minimize test variables. The results of the baseline tests are presented in Table 5-VI.

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<sup>1</sup> Phone conversation on January 18, 1995, with W. M. Pope, PERMEA, Inc., St. Louis MO.

Table 5-VI: Baseline M85 Emission Test Results

<b>Component</b>	<b>Average Emissions During Cold 505</b>
THC	0.962 g/mile
CO	7.287 g/mile
NO <sub>x</sub>	1.028 g/mile
METHANOL	5.047 g/mile
ALDEHYDES	0.366 g/mile

## 5.5 Vehicle Hydrogen Cold-Start Tests

The original test plan was to use stored hydrogen for cold-starting and to replenish the hydrogen used during the remainder of the federal test. This plan proved to be impossible for three reasons. First, during baseline testing, the average exhaust temperature downstream of the catalytic convertor was about 450°C. From our bench tests of the catalyst, this is approximately the temperature at which the decomposition reaction switches from net endothermic to net exothermic. Feeding methanol at this temperature could cause even higher temperatures and damage to the reactor. In addition, the hydrogen yield at this high temperature is poor and acidic condensates are produced. Reactor temperatures were controllable with exhaust air injection during earlier testing, but the degraded separator performance was uncorrectable. The carbon monoxide and methane in the separator product would have produced worse emissions than the baseline cold-start during the exhaust injection tests. For all these reasons, the hydrogen cold-start tests were performed with commercial bottled hydrogen.

Because the vehicle would be started with hydrogen, all the cold engine and starting enrichment tables in the ECM were disabled. The fuel tables were returned to their M100 calibration values, and the rest of the ECM functions were left with stock gasoline values.

The first set of tests began with a hydrogen cold-start and 20 second idle. During this time, the methanol injectors were disabled. Immediately before the first acceleration, the injectors were turned on, and the hydrogen was turned off. The remainder of the LA-4<sup>2</sup> cycle was performed with M100. The hydrogen flow during the 20 second idle was 45 slm, so 15 standard liters of hydrogen were consumed for this test. A carbon balance of the emissions with methanol reveals that 20.47 MJ of methanol was consumed in the test, but only 0.162 MJ of hydrogen was used (based on lower heating value). By comparing the % reduction in emissions with the % hydrogen used in the test, a leverage factor for the hydrogen use can be computed (see section 2.0 for a complete description of the concept of leverage). The emission results and leverage factors are presented in Table 5-VII. Note that these leverage factors are calculated from an M85 cold-start and would be much higher if repeatable M100 cold-starts could be performed.

<sup>2</sup> An "LA-4" cycle consists of Phase I (cold 505) and Phase II of the Federal Light-Duty Emission Test (FTP).

Table 5-VII: Average Emissions During Cold 505 - H<sub>2</sub> Cold-Start Only

<b>Component</b>	<b>Average Emissions During Cold 505</b>	<b>Leverage Ratio</b>
THC	0.276 g/mile	90.25
CO	4.732 g/mile	44.39
NOx	1.000 g/mile	3.34
Methanol	4.636 g/mile	10.30
Aldehydes	0.350 g/mile	5.46

The next set of tests were performed identically to the previous hydrogen cold-start tests, but with the addition of hydrogen for catalyst heating. During the ultralean idle period, extra hydrogen is injected into the exhaust stream ahead of the catalytic convertor. The unburned oxygen and extra hydrogen react initially on the catalyst surface, then a flame front develops in front of the catalyst. This extra heat is transferred very effectively to the honeycomb structure of the monolithic catalyst support. The catalytic convertor outlet temperature trace for the M85 baseline test is virtually identical to the hydrogen idle only test. However, the warm-up of the catalyst is very dramatic for the hydrogen injection test, as shown in Figure 5-2. A conventional M85 cold-start or hydrogen cold-start without exhaust injection requires 200 seconds to heat the catalytic convertor above 250°C, whereas the exhaust injection test needed only 55 seconds.

The total hydrogen flow for the exhaust injection tests was 130 slm; 45 slm idled the engine while 85 slm was injected into the exhaust. The equivalent heating power of the exhaust injection flow, based on lower heating value, is 15.1 kW. The emissions results from the exhaust injection tests are given in table 5-VIII. Again, the leverage ratios are calculated from an M85 baseline, so they very conservatively represent hydrogen cold-start improvements over pure methanol.

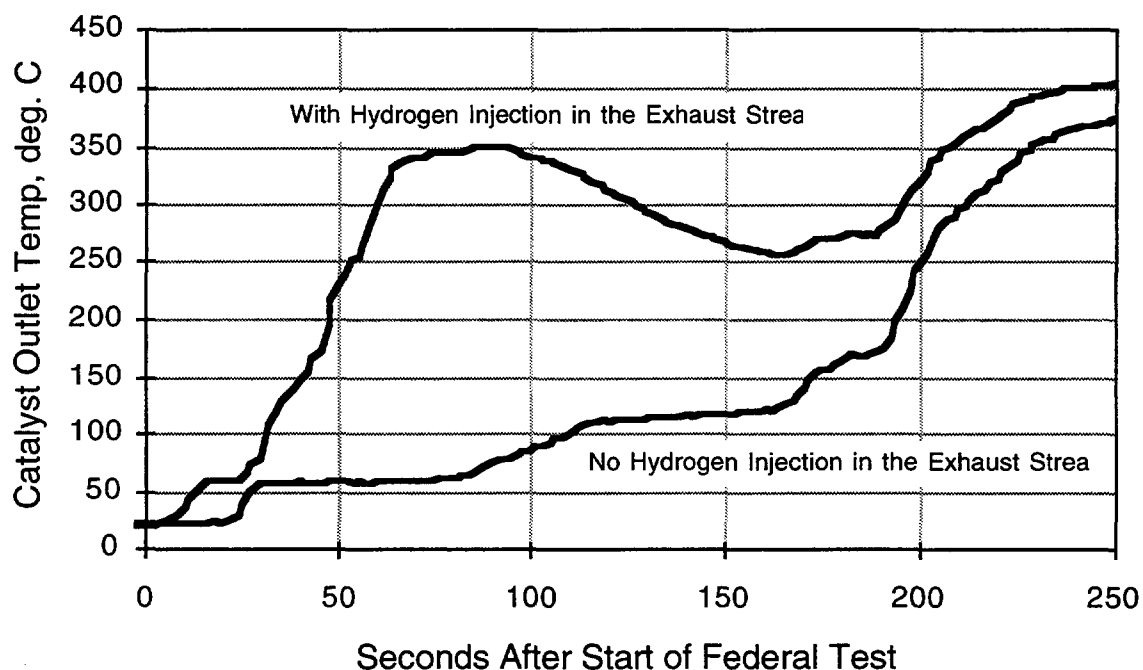


Figure 5-2: Average catalytic convertor outlet temperatures during hydrogen cold-start tests. The engine is started and idled ultra-lean for 20 seconds on hydrogen, followed by operation on M100 only. The warm-up during the M85 baseline is virtually identical to the M100 curve without exhaust injection above.

Table 5-VIII: Average Emissions During Cold 505 - H<sub>2</sub> Idle + Exhaust Injection

Component	Average Emissions During Cold 505	Leverage Ratio
THC	0.198 g/mile	35.61
CO	4.084 g/mile	19.71
NOx	0.849 g/mile	7.82
Methanol	1.195 g/mile	34.23
Aldehydes	0.299 g/mile	8.23



## 6.0 DISCUSSION OF RESULTS

The results of the emission tests are summarized in Figure 6-1. It is clear that a hydrogen cold-start improves unburned fuel and carbon monoxide emissions greatly. More than this, the ultra-lean engine operation allows direct chemical heating of the catalyst with hydrogen injection into the exhaust. By rapidly heating the catalytic convertor, further reduction of all the regulated emissions are possible. The percent emissions reductions were in all cases greater than the percent of total fuel energy represented by the hydrogen. Because the benefits are greater than the simple displacement of other fuels, this limited, discretionary use of hydrogen justifies the extra cost associated with its production and storage. The *leverage* ratios (percent emission reduction versus percent hydrogen from the total energy) are presented for each emission constituent in Figure 6-2. Because these values are calculated from an M85 baseline, they only conservatively represent the emission reductions possible for cold-starting a pure methanol vehicle with hydrogen.

A saturated air/methanol mixture approaches the lean flammability limit at about 11°C. Because methanol is difficult to cold-start at room temperature and almost impossible to start at very cold temperatures, the storage of hydrogen for starting provides practical benefits along with cleaner exhaust emissions. With proper hydrogen startup procedures (starter, ignition, and fuel sequencing) and ultra-lean engine operation, the vehicle never failed to start and idle, without backfires or abnormal combustion, throughout all testing.

The decomposition of methanol proved to be quite complex; the experience of CSM with dissociation catalysts provided a proven catalyst with good hydrogen yields, at controlled temperatures. However, the upper end of the exhaust temperature range produced less hydrogen and more secondary, exothermic products. The formation of acidic condensates at higher temperatures was unexpected, and the corrosive waste stream to the engine could not be tolerated with conventional materials. During testing at HCl, reactor temperature control was demonstrated with exhaust air injection. Another solution may be exhaust bypass valves, which were used on the SERI vehicles.

The self-heating nature of the reactions at higher temperatures may be a promising way to produce hydrogen without the exhaust heat exchanger requirement. If the acid formation can be controlled, an independent decomposition reactor may be started with electrical heat and maintained as long as the methanol feed is provided.

The polymer membrane hydrogen separators were very effective at separating hydrogen from binary  $H_2/CO$  mixtures. However, during testing with actual decomposed methanol products, the permeation of CO and hydrocarbons made the use of the permeate for exhaust injection tests impossible. Further tests with binary mixtures showed permanent damage to the separators' performance, which may have been caused by the organic and acidic components in the reactor product condensate.

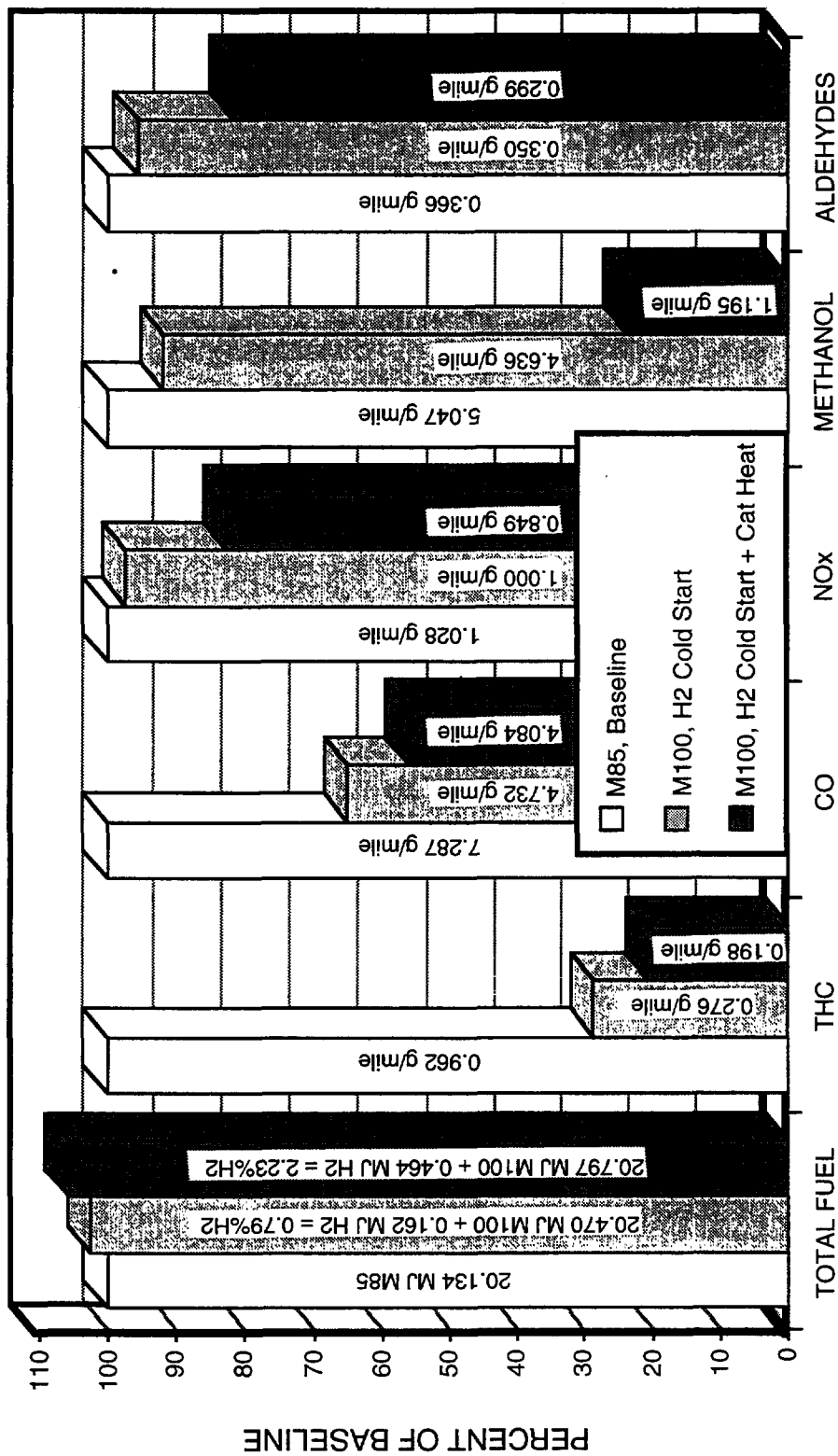


Figure 6-1. Comparison of Cold 505 tests: an M85 baseline test, an M100 test with the first 20 seconds of operation on pure hydrogen, and another M100 hydrogen cold start test with additional hydrogen injection into the exhaust to heat the catalyst.



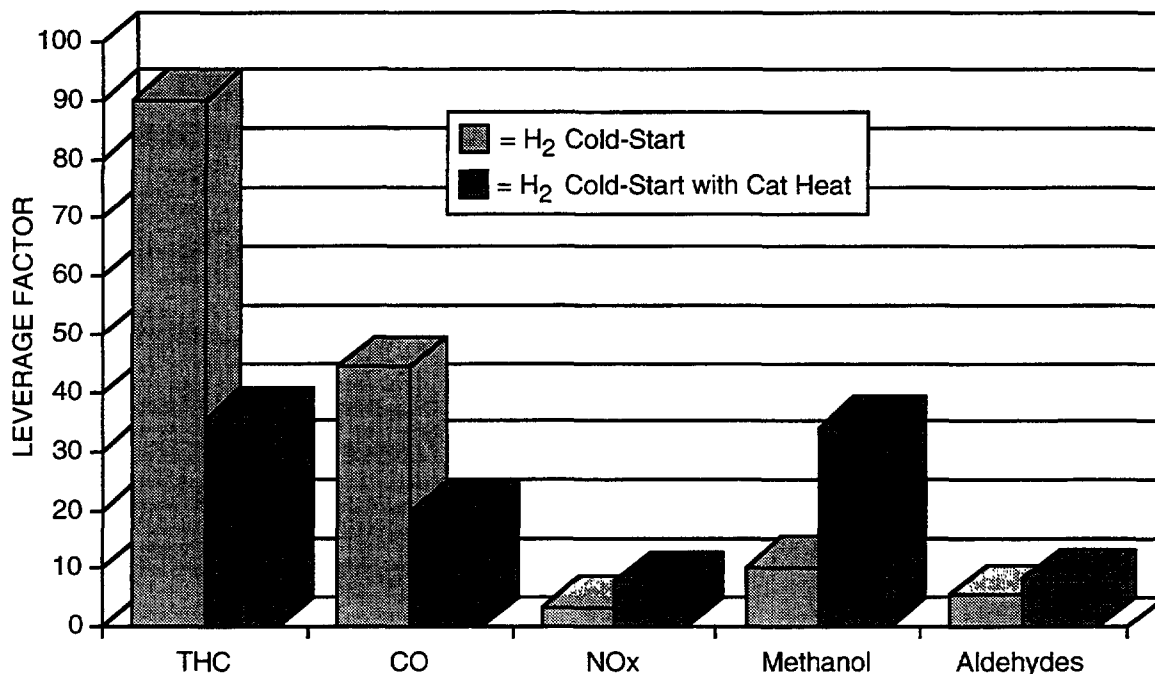


Figure 6-2: Leverage factors = % emission reduction ÷ % of fuel supplied as H<sub>2</sub>. Large leverage factors indicate highly effective use of hydrogen.

The approach used in the present work is sound except for the lack of an effective separation technique. Some of the objections to palladium separators that led to the selection of a membrane separator in this project are being addressed by work at CSM. Ultrathin films of palladium on a porous ceramic support may reduce cost and provide the structural support needed in automotive applications. Since palladium is also an effective dissociation catalyst, it may be possible to design the cracker and separator in one unit. However, purging residual hydrogen from the reactor would still be necessary to prevent hydriding as the reactor cools, which presents further complexity.

An alternative method of acquiring pure hydrogen onboard a motor vehicle is to electrolyze water with energy from the vehicle's electrical system. During decelerations, the electrical energy is virtually "free." This hydrogen production method could produce any reasonable pressure for storage, inherently solves the separation problem, and is independent of the primary vehicle fuel. However, a separate water container that must be filled regularly is required to keep the system working.



## 7.0 CONCLUSIONS AND RECOMMENDATIONS

- A hydrogen cold-start, followed by pure methanol operation during the first phase of the Federal Test Procedure, reduced the vehicle emissions by the following amounts when compared to an M85 baseline:

THC	71%
CO	35%
NO <sub>x</sub>	3%
Methanol	8%
Aldehydes	4%

- A hydrogen cold-start with exhaust injection, followed by pure methanol operation during the first phase of the Federal Test Procedure, further reduced the vehicle emissions by the following amounts when compared to an M85 baseline:

THC	79%
CO	44%
NO <sub>x</sub>	17%
Methanol	76%
Aldehydes	18%

- The above reductions were accomplished with only a small part of the total fuel energy supplied in the form of hydrogen (0.79% and 2.23%, respectively).
- When operating on hydrogen, the vehicle started with less cranking and idled smoother than with M85 operation; colder ambient temperatures would be expected to emphasize this benefit.
- With only 50% of the hydrogen recovered for storage, a reasonably small methanol dissociation reactor can provide enough hydrogen for a cold-start within 7 minutes of high-temperature operation.
- To produce good hydrogen yields, the temperature of the platinum-based dissociation catalyst must be controlled; this has been demonstrated by pumping controlled amounts of ambient air into the hot exhaust between the catalytic converter and the dissociation reactor.
- Polymer membranes proved to be very effective at separating hydrogen from carbon monoxide; however, the more complex product stream from an actual methanol dissociation reactor degraded the separators' performance.
- An effective hydrogen separation technique is fundamental to the hydrogen cold start concept because only hydrogen will react on the surface of a cold catalytic converter; any contaminants injected into the exhaust will pass right through the cold catalyst and become another source for harmful emissions.

- Hydrogen separation with palladium films on high-temperature substrates is being investigated at the Colorado School of Mines. Palladium separators provide higher hydrogen purity than any other technique, and palladium itself can be an effective methanol dissociation catalyst.
- Pure hydrogen could also be produced by water electrolysis; this technique would automatically separate the hydrogen and provide the pressure for storage.

## 8.0 RELEVANT LITERATURE

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